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EXFOLIATION AND MODIFICATION OF MOLYBDENUM DISULPHIDE

GOPIKA M S[1] & B. BINDHU[2]

[1]*Research Scholar, Department of Physics, Noorul Islam Centre for Higher Education, Kumaracoil, Tamil Nadu, India*

[2]*Professor, Department of Physics, Noorul Islam Centre for Higher Education, Kumaracoil, Tamil Nadu, India*

ABSTRACT

Two dimensional layered materials MoS_2 have attained an increasing scientific interest owing to its remarkable thermal, electrical and mechanical behaviours. Excellent property enhancement is possible on exfoliation of bulk MoS_2 into monolayers. In the present work the exfoliation of MoS_2 into a few layers is achieved by the use of a modifier CTAB. The treated MoS_2 is analysed using Fourier transform infrared spectroscopy. The presence of few layers is confirmed through TEM and SEM.

KEYWORDS: Modification, MoS_2, layered materials & Exfoliation

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Original Article

1. INTRODUCTION

Graphene have exceptional properties that giving rise to an extensive application of the material in many research fields. After graphene, there has been increased interest in the two dimensional layered materials. The Transition Metal Dichalcogenides and Metal Oxides have gained much importance. The transition metal in TMDs includes Molybdenum, Vanadium, Niobium etc and the chalcogens used were Sulfur, Selenium and Tellurium etc. The individual sheets are linked together by weak Van der Waals force [1]. Initially 2D graphene extraction was done using the scotch tape method and after that various exfoliation techniques with the aid of different chemicals were followed. Through these techniques Yao et al., [2] were able to produce graphene. The advantage in most of the layered materials is the strength of in-plane bonds in an individual layer and weakness of interaction between the layers due to Van der Waals force. This paves way for the separation of individual sheets having a good strength. This results in excellent property enhancement in an atomic level. Due to 2D structure, these class of material exhibit surface effects thereby paving way for suitable surface modification using different chemical surfactants. Most of them can be synthesised into nanoflakes and this enables its incorporation into other matrix material for the formation of composites with excellent properties [3]. Very small thickness of the material in an atomic scale enables the facile processing and application in electronic devices. The 2D layered materials may possess zero band gaps which can be exploited in optoelectronic devices. Most of them exhibit transparency, which finds application as electrodes in devices. 2D structures possess extreme strength which can be coupled with polymers for enhanced mechanical properties for a light weight applications.

In this work we have chosen MoS_2 which is a layered structure. MoS_2 is a TMD which overcomes most of the drawbacks possessed by 2D layered materials especially graphene. Unlike graphene MoS_2 possess the band gap which makes it excellent for electronic applications. It is used in energy storage, sensing and catalysis [3]. For the application of MoS_2 the bulk layered structure is to be exfoliated into two dimensional monolayers [4]. This resulted in the research on TMDs which are layered structures and can be exfoliated by techniques similar to that

of graphene. The general chemical formula for TMDs is MX_2, where M denotes transition metal and X stands for chalcogens. MoS_2 possesses remarkable properties like direct band gap, lubrication effect, catalyst property etc [5 - 7]. Radisavljevic et al., reported that the direct band gap of single layer MoS_2 is about 1.9eV, while the indirect band gap of bulk MoS_2 is around 1.2eV[8]. This change in the band gap of MoS_2 is possible because of the quantum confinement effect in the material.

The structure of MoS_2 is a sandwich layer of S-Mo-S, possessing strong bonds within the layers and each layer is being connected by weak Van der Waals interaction [9]. The weak interaction between the layers enables the easy exfoliation of the bulk MoS_2 into monolayers. There are different types of exfoliation techniques like covalent functionalization, [10] ultrasonication, [3] shear mixing [11] and addition of surfactants [12]. The main advantage in exfoliation of a layered material is an increase in the surface area of the material and this paves way for more nano effect in it [13]. Though MoS_2 was considered and used as a layered material, its importance and usage increased after the realization of the properties of 2D MoS_2 and this resulted in a lot of research in this area. The quantum size effect of MoS_2 is realized in its 2D from. Single MoS_2 sheet have a centrosymmetric structure, with Molybdenum atom sandwiched between Sulphur atoms. The material becomes highly inert to Oxygen or even liquids in this state. This is because of the absence of bonds at the edge of basal surface. A Strong intralayer bonding was accompanied by a weak interlayer bonding results in very good properties. The direct band gap of the material on exfoliation is exploited in the photoluminescent applications. The charge carrier mobility of exfoliated sheets is very less than the layered form. High dielectric material can be coated on the surface of the exfoliated sheets for increasing the mobility. This was done through the suppressing coulomb scattering effect. The material through certain treatments can be used in transistors, which are applicable in a sensing application. There are different techniques for the preparations of 2D exfoliated MoS_2 sheets [14]. The main approaches are bottom-up and top-down techniques. The solvothermal and CVD techniques are come under the bottom-up approach. The mechanical cleavage and the liquid phase exfoliation techniques are top-down approaches. Coleman proposed a method for the exfoliation of graphite that is free from the defect and which also can be useful in the exfoliation of other layered materials like MoS_2 [15]. In this method the graphite dispersed in a liquid is sonicated and graphene sheets are obtained in a large scale. The stabilization of the graphene sheets are done by the addition of some solvent or polymer or some surfactant. The sheets on analysis were known to be free from oxide. The dispersive state and exfoliation of different layered structure in various solvent were analysed by Cunningham et al., and it was found that the materials exhibited variation in dispersion state with a different solvents on ultrasonication [16]. Yao et al., reported the synthesis of two dimensional material in large quantities by the ball milling technique followed by ultrasonication of the samples [2]. The ball milling separates the sheets and the sonication process creates smaller crystal structures which are stable. May et al., [17] analysed the exfoliation and stabilization of the 2D layered materials in various polymers by dissolving them into two separate solvents. They evaluated the solubility parameter of all the three phases. It was found that the polymer is stabilized when the value of solubility parameter of the exfoliated sheets, solvent and polymer are the same. There are various chemical assisted the liquid phase techniques for the exfoliation of TMDs [18]. The different types of intercalation compounds formed out of this exfoliated structures were also discussed. The merits of the chemical technique over the other conventional methods for the preparation of intercalation compounds were also conferred.

After the exfoliation process the MoS_2 monolayers are more probable for restacking. In order to avoid this, the exfoliated MoS_2 sheets are to be properly modified using surfactants. It is also possible to incorporate guest species in

between the layers of MoS_2. While introducing the exfoliated MoS_2 into the guest species like polymers the uniform dispersion of the MoS_2 is very important, because the property enhancement solely depends on the homogeneous dispersion of the filler [19]. This can be achieved through the modification of MoS_2 with the suitable modifier. 2D MoS_2 can be a surface modified using certain types of surfactants. This results in stability of the MoS_2 layers. But the amount of surfactant incorporated while synthesizing is also to be considered, because too much of it may destroy the stability and the core properties of the material [20]. The addition of surfactant during synthesis of MoS_2 will result in sheets of larger surface area.

Cetyl Trimethyl ammonium chloride (CTAC) is one of the surfactant used in the preparation of MoS_2. The use of surfactant led to the exfoliation of MoS_2 sheets and the thermal stability of the material will also be increased [12]. The proper choice of the surfactant is most important because, the characteristic of the material may change drastically on its incorporation. The surfactant also has the ability to control the dimension and shape of the material on synthesis stage. Thus the presence of the surfactant will boost the exfoliation and modification of MoS_2 [20]. Tahir et al., investigated the effect of functionalising MoS_2 using polymer ligand [21]. Different types of precursors were discussed for functionalising with MoS_2 including some carboxylic acid which can be used for CNTs. The same technique can be used for functionalising TMDs, exploiting the weak Van der Waals interaction in between the layers of the material. The functionalization of MoS_2 was done using Nitrilotriacetic Acid (NTA) ligand and the same method can also be used for functionalizing other layered materials.

In this work we report that the liquid phase exfoliation and modification of MoS_2 using the modifier CTAB and the samples are analysed using Fourier transform infrared spectroscopy, TEM and SEM. The modified MoS_2 samples are coded as ct-MoS_2. The modification of MoS_2 using CTAB is done in different ratios. MoS_2 and CTAB in 1:1, 1:2 and 1:4 ratios are notated as 1 ct-MoS_2, 2 ct-MoS_2 and 4 ct-MoS_2 respectively.

2. EXPERIMENTAL

2.1 Materials

Molybdenum disulphide (MoS_2) (99% purity), Molecular weight 160.06g/mol is purchased from LOBA Chemie. N, N-Dimethylformamide (DMF) (98% purity) and Cetyl trimethyl ammonium bromide (CTAB) (98% purity), Molecular weight 364.45g/mol were obtained from Aldrich.

2.2 Exfoliation of MoS_2

Exfoliation of MoS_2 is done through the ultrasonication process. A known amount of MoS_2 is added in the solvent DMF and is mechanically stirred for about 30 mins. The stirred solution is ultrasonicated with a bath sonicator for 8 hrs. Ultrasonication destructs the weak force in between the stacked MoS_2 sheets thereby converting the bulk MoS_2 into nanoflakes. The solution is then centrifuged at 4000 rpm for 10 mins and the product obtained is then dried at 60ºC in vacuum oven.

2.3 Modification of MoS_2

A colloidal suspension of exfoliated MoS_2 and DMF was prepared. Cetyl trimethyl ammonium bromide solution is prepared by dissolving CTAB 100 ml of water and the solution is added into MoS_2 suspension while stirring and

maintaining a temperature of 60°C for 8 hrs. Obtained solution is then centrifuged for 8 mins at 4500 rpm. Hot water is used to wash the same for the removal of Bromine. The product is then dried in vacuum at 60°C for 24hrs.

2.4 Characterization

The FTIR spectroscopy was employed for the identification of various functional groups in the exfoliated MoS_2 nanoflakes. Fourier transform infra-red spectroscopic (FTIR) analysis of the samples was obtained from Nicolet (MAGNA 550). The measurement was done at the room temperature at the scanning range of 400–4000 cm^{-1}. Calibration is performed using the KBR pellet. SEM analysis of the samples are done using FEG-SEM, JSM-7600F at 10 kV accelerating voltage. The dried samples were dispersed in the water and a droplet of the solution is spread on a silicon wafer and is dried. The dried wafers were sputtered with gold and then examined under SEM. TEM analysis of the samples was done on a Field Emission Microscope, JEOL JEM-2100 F, Japan. The dried samples were dispersed in the water and a droplet of the solution is spread on the grid of the TEM and dried. It is then examined under TEM.

3. RESULTS WITH DISCUSSIONS

3.1 FTIR Analysis

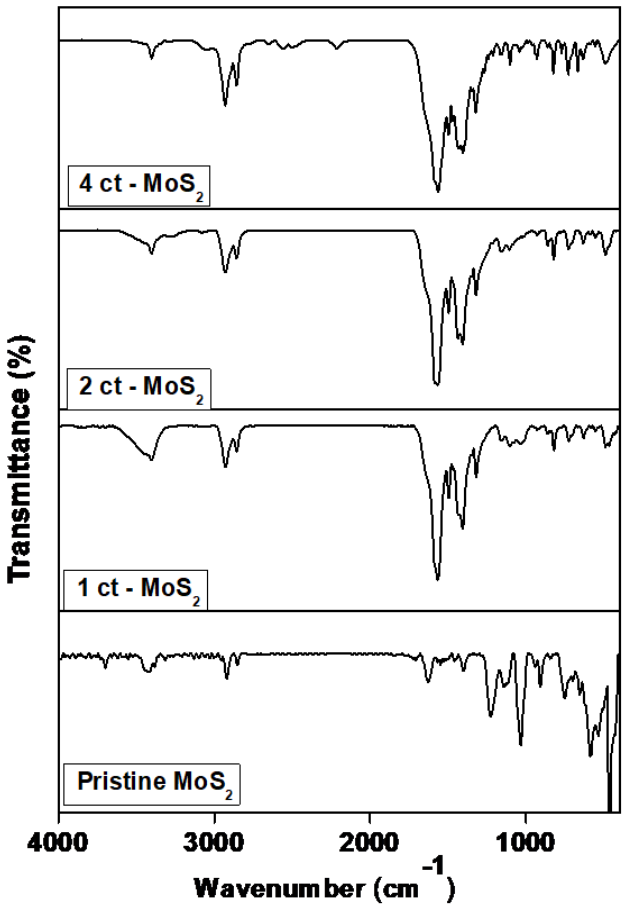

Figure 1: FTIR Spectra of Neat MoS_2 & ct MoS_2 Samples.

The FTIR spectra of pristine MoS_2, 1 ct-MoS_2, 2 ct-MoS_2 and 4 ct-MoS_2 are as shown in figur 1. The spectra show that all the characteristic peaks of MoS_2. The FTIR peak at 3422 cm^{-1} which appears in almost all the spectra correspond to OH stretching vibration [22]. Double peak at 2923 cm^{-1} and 2846 cm^{-1} corresponding to antisymmetric

and symmetric stretching vibrations -CH_3 and -CH_2 group of the CTAB molecule [23]. The increase in peak intensity confirms the presence of the CTAB in the modified MoS_2. The peaks at 1308 cm^{-1} are assigned to C-N stretching of the amine group. The peaks at 1108 cm^{-1} and 820 cm^{-1} corresponding to C-H bending vibrations. The peak at 1385 cm^{-1} corresponding to C-H aliphatic C-H bond [24]. The peak formed in CTAB modified MoS_2 at 724 cm^{-1} is due to the δ_{C-H} bending of the -CH_2 group. Thus, correlating the results obtained by Chhetri et al., the presence of long alkyl group in the CTAB modified material is confirmed [25]. There is a strong peak at 1564 cm^{-1}which is due to the absorbance of the -NH_2 vibration. Thus the CTAB modified MoS_2 has all the vibrations corresponding to the -CH_2 and -CH_3 group of the modifier, which proves that the modifier is well adsorbed on to the surface of exfoliated MoS_2 sheets.

3.2 SEM Analysis

Morphological observation of Pristine MoS_2 and ct-MoS_2 at different filler concentration were made using SEM analysis. Fig 2 gives the FESEM images of pristine MoS_2, 1ct-MoS_2, 2ct-MoS_2 and 4ct-MoS_2 respectively. From the SEM investigation the degree of exfoliation can be understood. Fig 2 (a) shows the SEM image of pristine MoS_2. It is clear from the figure that the SEM image of pristine MoS_2 shows stacked MoS_2 layers with large thickness. The exfoliation starts from 1 wt% addition of CTAB as seen in Fig 2 (b). In the 4 ct-MoS_2 sample as in Fig 2 (d), few layer flakes are visible. The effectiveness of exfoliation of the pristine MoS_2 into few layers can be attributed to the modification of MoS_2 using CTAB.

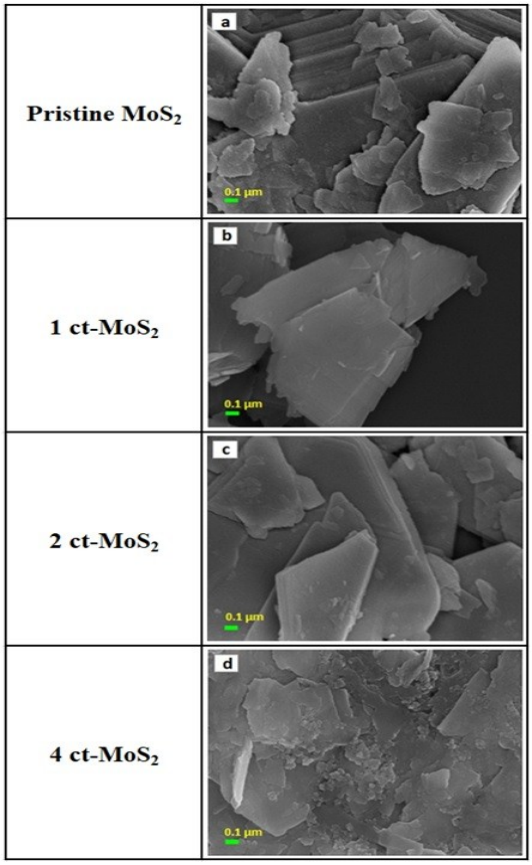

Figure 2 : FESEM of a)Pristine MoS_2, b) 1 ct-MoS_2, c) 2 ct-MoS_2 & d) 4 ct-MoS_2

3.3 TEM Analysis

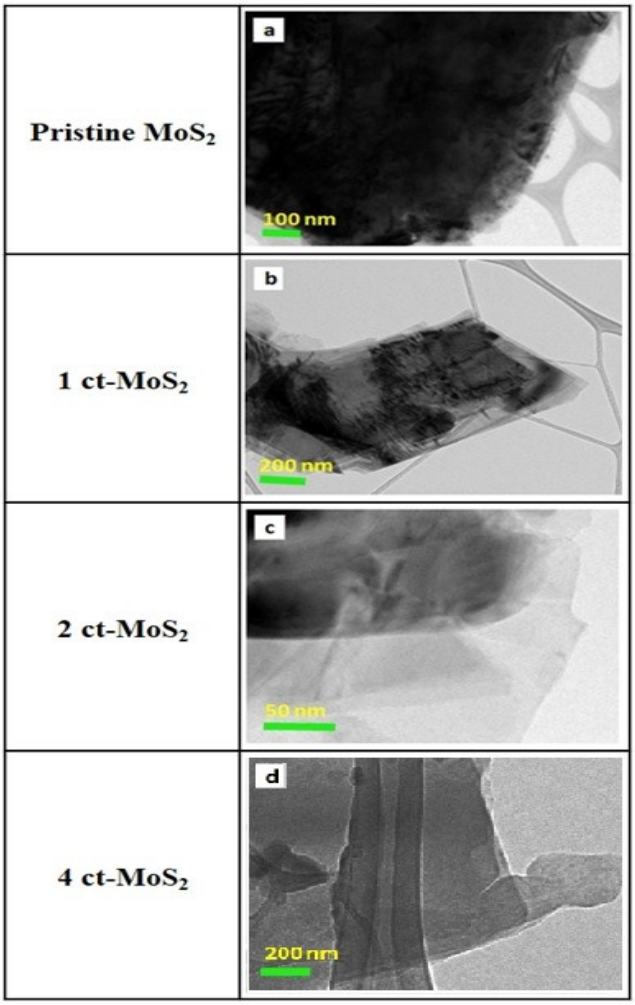

Figure 3: TEM of a) Pristine MoS_2, b) 1 ct-MoS_2, c) 2 ct-MoS_2 and d) 4 ct-MoS_2

Exfoliation of the bulk MoS_2 into monolayers was clearly understood from the TEM analysis. TEM images of Pristine MoS_2, 1 ct-MoS_2, 2 ct-MoS_2 and 4 ct-MoS_2 are shown in figure 3. Exfoliation of the pristine MoS_2 into few layers was clearly understood from the TEM analysis. Figure 3 (a) shows the TEM image of pristine MoS_2. It is an evident that the pristine MoS_2 shows well stacked layers and thereby it is opaque to the electron intensity. The exfoliation is initiated from the addition of CTAB at 1wt % and the thickness of the layers seemed to decrease compared to that of the pristine MoS_2. At 4 wt% loading of CTAB as shown in figure 3 (d) the sheets seems to be exfoliated to some extent compared to that of pristine MoS_2.

4. CONCLUSIONS

The exfoliation and modification of bulk MoS_2 is done by the inclusion of CTAB. The modified MoS_2 is a good candidate as the filler in polymer composite, because of its compatibility with the polymer matrix. This will also helps in the homogenous dispersion of MoS_2 in the polymer which results in property enhancement. The prepared samples were studied using FTIR from which the vibrational peaks were identified. From the obtained peak values it can be concluded that the organic modification of MoS_2 by CTAB has happened. The samples were also examined by SEM and TEM. The

SEM results depicted the visible exfoliation of the bulk MoS_2 sheets on maximum modifier concentration. It is also supported by the TEM analysis in which transparency of the MoS_2 sheets towards electron beam can be seen at modification of MoS_2 using 4 wt% CTAB. This proves the formation of ultrathin MoS_2 sheets.

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AUTHOR'S PROFILE

Gopika M S M.Sc., M.Phil., is a Research Scholar in Physics. She is pursuing her research in the field of nanocomposites under the guidance of Dr. B Bindhu in the Department of Physics, at Noorul Islam Centre for Higher Education, Kumaracoil, 629180. She has completed her M.Sc and M.Phil in Physics from Manonmaniam Sundaranar University, Thirunelveli. She has published 5 research papers in her field of research.

Dr. B. Bindhu M.Sc., Ph.D., has 13 years of teaching experience. Her areas of interest are in the field of Nanomaterials, Bio-Polymers, Nanocomposites, Smart materials and Crystal Growth. She has received her doctoral degree from

Manonmaniam Sundaranar University, Tirunelveli. Currently she is working as a Professor in the Department of Physics at Noorul Islam Centre for Higher Education, Kumaracoil, 629180. She has published more than 22 papers in national and international journals.